AN ABSTRACT FROM THE THESIS OF:

Jeffrey C. Perkins in partial fulfillment for the Masters of Science Degree in Physical Sciences presented July 14, 2000. Title: A STUDY OF CHEMICAL AND PHYSICAL PROPERTIES OF THE GROUND WATER AND SURFACE WATER AT ROSS NATURAL HISTORY RESERVATION AND KAHOLA LAKE IN EAST- CENTRAL KANSAS

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Water properties in limestone aquifers and surficial water bodies vary spatially and temporally dependent on factors such as precipitation, recharge rates, groundwater flow rates, joint patterns, antecedent conditions. and anthropogenic activities. This study involved sampling and testing selected chemical and physical properties of the ground and surface water at two locations in east central Kansas. At each location a surface water body and one spring was chosen for sampling. Multiple samples were collected from each location at different times dependent on climatic conditions. Remote sensing and field studies were also used to evaluate factors that could be affecting water quality at each study locale.

The primary sampling location was the Ross Natural History Reservation (RNHR). At this location Gladfelter Pond and Ross Spring were chosen for sampling. The second sampling location was in the vicinity of Kahola Lake. The Lake and a nearby spring were chosen for sampling. The duration of the study

was from the fall of 1999 through winter 2000, and the field procedures consisted of three rounds of sampling and water analysis at the four sites. The chemical and physical properties determined from sampling and testing were water temperature, pH, calcium, alkalinity, CaCO₃, chloride, zinc, orthophosphate, and nitrate/nitrite ($NO₂$ and $NO₃$ as N). Ninety-six separate analyses were performed.

In an article entitled Flint Hill Springs (Sawin et. al. 1999) states that "In general, water quality and flow rates in the Flint Hills springs have remained steady through the years". I investigated for indications that water properties changed temporally in spring water at a different rate than the surface water at each location. The basic premise was that spring water should be more resistant to change than surface water bodies. My results indicated that most of the ground water properties exhibited greater changes than the surface waters sampled at the same locations. Despite the limited time frame of this study I believe that my findings indicate the "steady-state" image about springs is misleading. The only test that appeared to support the steady state picture of the Flint Hill Springs was temperature because of the earth's geothermal properties.

Another goal of the study was to evaluate concentrations of zinc, nitrate, and orthophosphate with respect to State of Kansas drinking water standards. Concentrations of zinc and nitrate were well below State of Kansas drinking water maximum contaminant levels. Orthophosphate levels were also generally low, however, a spike in concentration was observed in one sample from Gladfelter Pond at the RNHR during the second round of testing.

A STUDY OF CHEMICAL ANI) PHYSICAL PROPERTIES OF THE GROUND WATER AND SURFACE WATER AT ROSS NATURAL HISTORY RESERVATION AND KAHOLA LAKE IN EAST- CENTRAL KANSAS

A Thesis

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In Partial Fulfillment

Of the Requirements for the Degree

Master of Science

By

Jeffrey Charles Perkins

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Chapter One

Introduction and Background

Section 1A: Introduction

It was the purpose of this study to examine chemical and physical properties of ground water and surface water at two locations in east central Kansas. The two locations chosen for study were the Ross Natural History Reservation (hereafter abbreviated RNHR) and the Kahola Lake area. Both locations have surface water bodies and springs that could be sampled easily.

There were several major parts of this study. The first part included a background investigation of previous studies of water quality in the area and acquisition of relevant data sets to be used in the analysis phase of the project. The principal source for water quality data was a Masters Thesis entitled Water Quality in Lake Kahola And Adjacent Domestic Water Wells by Thomas Peterson (1992). Precipitation data was acquired for a period of time prior to the first water sampling date through the duration of the study. This data was acquired from the National Climatic Data Center that is maintained by the National Oceanic and Atmospheric Administration (NOAA). This data was to be used to help understand relationships between precipitation and various water properties. Another major component of the background investigation involved the acquisition of various spatial data sets called coverages to be used to create various views of the study area. Individual coverages depicting drainage basin divides, river locations, cities, and county boundaries were acquired from Data

Access and Support Center (DASC) at the Kansas Geological Survey, in Lawrence Kansas.

The next part of this investigation consisted of field studies. This included water sampling, field measurements of water temperature, evaluations of limestone joint patterns, description of topographic relief, and kite aerial photography at RNHR.

The last major component of this investigation involved laboratory analysis of the collected water samples. These tests were performed in the Jones Environmental Chemistry Laboratory Suite of the Science Hall, at Emporia State University. The specific tests performed were pH, calcium, alkalinity, CaC03, chloride, orthophosphate, nitrate/nitrite $(NO₂⁻$ and $NO₃⁻$), and zinc.

The analysis phase of the study required the compilation of the total data package into a useable form for comparisons. Comparisons were accomplished largely by graphing the results of laboratory and field analysis for interpretation of the data on an absolute and relative basis. The four specific goals of the field, laboratory and comparative analyses in this study were as follows:

- 1) Examine the differences in selected chemical and physical water properties between Gladfelter Pond and Ross Spring at RNHR.
- 2) Compare the results from RNHR with results from another location in the same region. Kahola Lake and a nearby spring were selected for this comparison.
- 3) Check for chemicals that should not be present naturally in surface and ground waters of the Upper Neosho River system.
- 4) Evaluate the changes in chemical and physical water properties caused by factors such as precipitation.

Section 1B: Regional Hydrologic Background:

This study was conducted in the headwaters region of the Neosho River drainage basin in east-central Kansas (Figure 1). This system merges with the Arkansas River just north of Muskogee, Oklahoma. These waters then feed into the Mississippi River in Arkansas and ultimately flow into the Gulf of Mexico. Since much of this region relies on lakes and reservoirs for drinking water, surface water quality is an important issue throughout the region.

Kansas Rivers, Drainage Basin Divides, and Political Bounderies In Reference To Study Location

Figure 1: Region of StUdy in Kansas. This area of the Neosho River Basin displays a dendritic pattern with streams generally flowing from the west to east then gradually turning in a southeast direction. This drainage off the eastern side of the Flint Hills produces topography with low rolling hills interspersed with low-lying floodplains that flank the meandering Neosho River and its tributaries.

In addition to the surface water features mentioned in the previous paragraph there are significant local and regional aquifer systems in the region. Groundwater flow patterns through these limestone aquifers are controlled by two principal factors. The regional bedrock dip is the primary control on the direction of groundwater movement in much of the region. Most strata in the study area exhibit a gentle slope downward to the west-northwest at a rate of 4 to 8 meters per kilometer (Peterson '92). Since groundwater tends to move in the direction of dip, most flow is to the west-northwest unless the dip of the rock strata has been affected by local structural features. The other significant control on water flow through these limestone aquifers is the orientation of the joints that provide conduits for recharge and lateral ground water flow. Joints in resistant limestones produce zones of weakness that are preferentially weathered and eroded. Since streams and groundwater have an easier time eroding or dissolving material along these zones of weakness stream channels and groundwater flow patterns tend to preferentially follow the regional joint patterns.

Section 1C: Local Geo-referencing

The RNHR and Kahola Lake are located near the junctions of Lyon, Morris and Chase counties west of Americus, Kansas (Figure 2). The locations of the Cottonwood Falls and Emporia NW Weather Stations are also noted on the map for consideration later in this study. It can also be noted that both the RNHR and Kahola Lake are located to the southwest of the Neosho River Valley within the Flint Hills physiographic province.

Figure 2: Modified local area map of Geology, Geomorphology, and Geohydrology of the Flint Hills, East - Central Kansas by Dr. James Aber (1999).

Section 10: Regional Bedrock Geology:

Kahola Lake is located to the west-northwest of RNHR (Figure 2). The general bedrock age decreases from east to west within this region indicating that the rock units are dipping to the west. The ages of the rock units are therefore younger at Kahola Lake than at RNHR due to this regional trend. All of the rock units at the two study locales are part of the Council Grove Group, Wolfcampion Series, of the Permian System (Figure 3).

Figure 3: Stratigraphic sequence of bedrock in the study areas. Adapted from Lutz-Garihan and Cuffey (1979, fig. 3)

These bedrock units consist of interbedded, highly-jointed, and fractured limestones, cherty limestones, and shales that are usually gray, green, or red. The sequences of sediment that eventually became these bedrock units were deposited as the Permian Seas in Kansas advanced and retreated. The packages of red and green shales are indicative of shifts between reducing (green) and oxidizing conditions (red) either at the time of deposition or in postburial diagenic environments. Both the shales and limestones in this region show the effects of weathering where exposed at the land surface.

In an article by Burchett et. al. (1983) the major lineaments (Figure 4) or linear features observable at a regional scale were described. These lineaments are a reflection of crustal structures such as fault lines that are believed to correspond with the regional bedrock joint sets.

Figure 4: Lineament map of east - central Kansas. The lineaments correspond to the regional bedrock joint sets. Many of the major lineaments in the study region follow the same trend as the Neosho River valley (labeled N). Adapted from Burchett et. al. (1983, Plate 3).

Typical limestone beds in the study region display a blocky appearance caused by erosion where these relatively brittle rocks have separated and weathered along joint sets. These joint sets are created or accentuated when these limestone beds undergo even minor tectonic activity such as uplift and/or compression (Figure 5). Such minor tectonic events have occurred in this region in the geologic past. The most notable evidence for this can be found along the Nemaha uplift that is just to the west of the study region.

Section 1E: Background of the Ross Natural History Reservation and Kahola Lake:

The Ross Natural History Reservation is an approximately 200-acre tract of land located in Lyon County that was donated to Emporia State University as a natural reserve to study many different physical and biological systems by F. B. and Rena G. Ross in November 1958. The original purpose was to; "..provide the Kansas State Teachers College (now Emporia State University) with a location for students and faculty to perform research and field studies, aid in the teaching of the biological sciences, and enable a segment of the tall grass prairie ecosystem to be preserved" (Spencer 1979 after Hartman 1960).

Prior to the establishment of the reservation there were two distinctive land use practice categories at the site. The first category of landuse was native grass pasture that was use to graze livestock but was never plowed. The second category of land use involved row crop agriculture. These cropland tracts have undergone the normal process of plant succession after cultivation ceased prior to 1960 (Spencer 1979 after Hartman 1960) and are now covered by grasses and forbes similar to the surrounding pasture lands.

Kahola Lake was constructed as a result of the need for a more stable water supply for the City of Emporia. This need was recognized during the early 1930's when drought conditions prevailed throughout the area. Kahola Lake was constructed with assistance from federal financing in the form of a work relief project. Kahola Dam was completed across Kahola Creek in 1937. This mainly earthen structure has limestone blocks on the upstream side to prevent wave

erosion. These limestone blocks were cut from local formations and laid by hand. Kahola Lake now has about 200 cabins on lots flanking the lake's perimeter that are occupied both seasonally and year round. Currently Kahola Lake's primary function is recreation. It does, however, still serve as an emergency water supply for the City of Emporia.

The primary land use around the Kahola Lake study locale and the RNHR is agricultural. Native grass pasture for cattle is the dominant land use on hilly uplands while grain fields are more common on flat, lower-lying fields occupying floodplains locations.

Chapter Two

Water Sampling and Analysis

Section 2A: The Four Goals of the Water Analysis:

- 1) Examine the differences in selected chemical concentrations in the waters of Gladfelter Pond and Ross Spring at RNHR.
- 2) Compare the RNHR values with concentrations measured in waters sampled at another location in the region.
- 3) Check for a number of chemicals that should not be present in high concentrations naturally in the Upper Neosho River system that may indicate either natural or anthropogenic pollution.
- 4) Compile data into graphical form for comparative analysis of the test results.

Section 28: Sampling Sites:

At Ross Natural History Reservation, Gladfelter Pond was chosen as the surface water sampling site and Ross Spring was chosen as the ground water sampling site. Gladfelter Pond is a relatively small water body whose dam was constructed across an ephemeral stream that drains surface water from lands currently used for pasture or which are part of the RNHR (Figure 6). Ross Spring emanates from a small outcrop of the Neva limestone northeast of the buildings at RNHR (Figure 7).

Figure 6: Gladfelter Pond as viewed from the northwest. The pond's water level and volume are low due to late August through November drought conditions. The was created by constructing an earthen dam across an ephemeral stream channel. Photo by Dr. James Aber, November 1999.

Figure 7: Ross Spring photographed by the author and Dr. James Aber using kite aerial photography, November 1999.

To satisfy the second goal of this study, an additional sampling location was selected to compare the chemical concentrations found at the RNHR with concentrations measured at another location in the same region. Kahola Lake (Figure 8) was chosen for several reasons:

- 1) Previous water test data from this site were available.
- 2) The lake is part of the same Neosho River drainage basin.
- 3) Ready access to sample sights including numerous springs.
- 4) The lake is a valuable water resource.

Figure 8: Panoramic photo of Kahola Lake nestled in the native grassland used to graze cattle. Photograph by author 1/5/2000.

The relative positions of the two Kahola Lake region sampling sites can be seen in Figure 9. The two specific sampling sites within this area were Kahola Lake at the end of a dock located at cabin 93 belonging to Dr. James Aber and his wife, Susan (Figure 10), and Kahola Spring at a small outcrop of the Eiss limestone on the southeast bluffs overlooking the lake (Figure 11).

Figure 9: Kahola Lake aerial photograph modified from a United States Geological Survey photo. The Kahola spring sampling site is on the cliffs on the southeast side of the lake due to the local dip being to the northwest (317 $^{\circ}$) at an angle of \sim 0.280 degrees (Peterson 1992).

Figure 10: Kahola Lake sampling site photographed by author 1/5/2000.

Figure 11: Kahola Spring sampling site. The water from this spring flows down a small gully into the lake. Photograph by author 1/5/2000.

The springs at Kahola Lake and the RNHR are contact springs (Figure 12). The springs at Kahola Lake are a result of the highly jointed and fractured Eiss Limestone member resting on top of the relatively impermeable Sterns Shale. At Ross Spring the highly jointed and fractured Neva Limestone is resting on top of the Salem Point Shale. In both cases surface waters infiltrate and ground water flows along the fractures and joints in the limestones. Flow directions are a function of the direction of dip for the underlying relatively impermeable shales.

Figure 12: Diagram of the contact spring geologic structure system in operation at Kahola and Ross Springs. Diagram from Sawin et. al. (1999, figure 4).

Section 2C: Sampling Schedule and Antecedent conditions:

In mid - October 1999 a sampling and testing trial run to check the physical process of sample collection, handling (including preservation techniques, time frames, and storage) and testing procedures was performed. It was found that at both spring locations a 250 mL. bottle was needed for sample collection due to limited space between the bottom of the spring and the point at which water was flowing from the strata. The other sampling, handling and

testing procedures were thought to be adequate at the times the samples were being collected.

It was my desire to perform my testing based on climatic conditions rather than a fixed schedule. The primary weather factor influencing the volume of discharge of ground water from the springs and runoff into surface water bodies was thought to be precipitation. Therefore, it was thought that precipitation might also affect water chemistry. So, the initial sampling was performed after an extended period of apparent drought based on observations of soil conditions and water flow in local streams. The subsequent rounds of sampling were performed after varying intervals of time following measurable precipitation events. The basic hypothesis was that water chemistry should vary somewhat with the timing, volume and duration of precipitation.

The second general hypothesis to be tested by the sampling and laboratory analysis was fairly simple. It was expected that there would be more variability in water chemistry in surface water bodies than in groundwater discharging from springs. This idea was based in large part on a statement by Sawin et al. (1999) that "In general, water quality and flow rates in Flint Hills springs have remained steady through the years".

To establish the antecedent conditions for each sampling period and evaluate the possible effects to the aquifer and surficial hydrologic systems of precipitation events, graphs were generated for the thirty-day period prior to each sampling date. These graphs show precipitation amounts on a daily timeframe. The precipitation data for both Cottonwood Falls.and Emporia NW weather

stations were used for the graphs because they were the nearest stations. These data sets were obtained from the National Climatic Data Center of the National Oceanographic and Atmospheric Administration. The results were entered into Excel spreadsheets and graphed.

The first official sampling date was November 11th, 1999. At that time the soils displayed significant shrinkage cracks and the local streams as well as the springs had greatly reduced flow. Figure13 displays the precipitation graph for the 3D-day period previous to the first round of sampling. Notice that the last precipitation event before sampling occurred 11 days prior to the sample date.

Precipitation - 30 Day Period Prior to 1st Round of Testing

Figure 13: Thirty-day precipitation graph prior to the first round of sampling.

The second round of samples were collected on January 5th, 2000. Both of the springs displayed a higher discharge and the lake levels were slightly higher. The shrinkage cracks seen earlier in the soil had essentially disappeared. Figure 14 is the graph of precipitation for the 30-day period previous to the second round of sampling. Notice that there were five individual precipitation events measured in the 30 days prior to sampling. Two of these approached or exceeded a depth of one inch (2.54cm).

Precipitation - 30 Day Period Prior to 2nd Round of Testing

Figure 14: Thirty-day precipitation graph prior to the second round of sampling.

The third round of samples were collected on February 7th, 2000. Figure 15 contains a graph of precipitation for the 30-day period prior to the third round of sampling. Notice that only one precipitation event was recorded at the

Cottonwood Falls station while three events were recorded at the Emporia NW station. Another important aspect of these precipitation events was that they were comprised in large part of frozen forms, sleet, snow, or freezing rain. At the time of sampling it had been at least 10 days since the last precipitation event but there was a two to three day period when melting occurred. At this time there was an obvious increase in flow in local streams and the springs appeared to be discharging more water.

Precipitation - 30 Day Period Prior to 3d Round of Testing

Figure 15: Thirty-day precipitation graph prior to the third round of sampling,

Section 20: Laboratory Analysis Flowchart:

The following tests were performed on each sample from each sampling site for

all three rounds:

Figure 16: Testing Flowchart. Diagram *by* author fall 1999

The tests for free calcium ions, alkalinity, and $CaCO₃$, were to evaluate the differences between the surface and ground waters as a function of recharge, dissolution of the bedrock, and dilution. The tests for chloride, nitrate/nitrite, orthophosphate, and zinc were specifically intended to look for possible contamination by either anthropogenic or natural sources.

Section 2E: Sampling Methodology:

It was determined through the testing flowchart that 500 ml of sample was needed for each set of analyses. Therefore, for each round of sampling four 500 mL plastic bottles were washed with dilute HCL, rinsed three times with tap water, three times with type 1 water, allowed to drain, then capped. A smaller 250 ml bottle was also prepared in the same manner to facilitate collection at the springs where it was found during the trial collection that space was an issue with the larger bottles. Once the two bottles were thoroughly rinsed with water from the source and drained, the actual samples were collected by filling the smaller bottle then transferring that solution to the larger bottle until full. The temperature was measured in the field with a laboratory grade glass thermometer then a label was affixed to the bottle with location, temperature, time, and date recorded on each bottle. To further assure the prevention of sample switching, each sample was inserted into a pre labeled plastic zip lock bag and placed in an ice filled cooler to retard or stop chemical changes to the sample in transit.

Section 2F: Testing Methodology:

The tests were performed in accordance to procedures taken from: Standard Methods for Examination of Water and Wastewater, 19th ed. Eaton, Andrew; et. all (1995). Each test/measurement is described below in detail.

Temperature:

It was the purpose of the temperature tests to show the differences in heat energy loss rates to the atmosphere by the two surface water bodies (Gladfelter

Pond $-$ a relatively small body, and Lake Kahola - a much larger body) and the two aquifers. The same laboratory grade alcohol thermometer, a Fishbrand (catalog number 14-997) was used in all temperature readings. To ensure the most accurate field temperature readings possible, the plastic sample bottle and thermometer were in all cases rinsed with and allowed to sit in the water being sampled for several minutes before the actual reading was recorded. After the sample bottle was refilled the thermometer was reinserted and allowed to sit in the solution about two minutes before the taking the final reading.

pH:

The principle behind testing for pH is to determine the numerical value of the negative logarithm (base 10) of the activity of the hydronium cations of a solution, or simply put how basic or acidic a system is. The test for pH was performed by probe analysis by potentiometry at Emporia State University. The maximum holding time of the samples was listed as 2 hours. During testing, this time limit was met for all samples. The instrument used during this testing was a Denver Instrument Basic, model 11341. To prevent carry over contamination the probe was thoroughly rinsed with type 1 water between tests.

Alkalinity:

The principle behind the alkalinity test is to measure solutions ability to neutralize acid. In natural environments with a pH < 9, this capacity is due almost entirely to $HCO₃$. It can be assumed in this region of this study due to the limestone bedrock that $HCO₃$ is the primary buffering agent in these water

systems. The source of the $CO₃⁻²$ anion is the CaCO₃ weathered from the limestone bedrock.

Alkalinity is measured by titration with a standard acid to the pH at which $HCO₃$ is converted to H₂CO₃. Bromocresol green indicator is used and it has a color change from blue to yellow green in this pH vicinity. The primary standard was 0.0250 M sodium carbonate (2.560 g oven dried reagent grade $Na₂CO₃$ in 1000 mL of Type 1 water). The secondary standard (titrant) was 0.020 M HC/. All titrations were performed in duplicate.

Testing Procedures:

- 1) All beakers, flasks, pipettes, and burettes were rinsed with dilute HCI, three times with tap water, then three times with type 1 water. Titrant was added to the burette and affixed into the stand above the magnetic stirrer.
- 2) The 250 mL dry ertimeyer) flasks were filled (after being tarred) in the following manner with the weight recorded at each step; Flasks 1a & 1b) \sim 100 mL Type 1 water and 6 drops of indicator each

Flasks 2a & 2b) ~ 10 mL Na₂CO₃ standard, 6 drops of indicator, and filled to \sim 100 mL with Type 1 water each Flasks 3a & 3b) \sim 100 mL Gladfelter Pond Sample and 6 drops of indicator

each

Flasks 4a & 4b) \sim 100 mL Ross Spring Sample and 6 drops of indicator each

Flasks 5a & 5b) \sim 100 mL Kahola Lake Sample and 6 drops of indicator each

Flasks 6a & 6b) \sim 100 mL Kahola Spring Sample and drops of indicator each

- 3) After insertion of the rinsed magnetic capsule, the flask was placed on the stirring platform.
- 4) Titrant was added from the burette until the blue color had completely disappeared replaced by a yellow green color. This represents a pH endpoint of about 4.5.
- 5) The replicate sample was titrated. If the titrant volume did not agree within 0.2 mL, a third trial was performed.
- 6) With the unknowns, if the weight of sample / volume of titrant used ratio did not agree within 2%, a third trial was performed.

Calcium:

The tests for calcium content were all performed with a flame atomic absorption Perkin-Elmer AAnalyst model 100. To reach the optimum operating temperature for this procedure, all manual settings such as burner height and air/acetylene mix were adjusted to the maximum absorbance readings using a standard each time a test was run. The settings and ranges for these tests were;

Wavelength = 422.7 nanometers

Slit Width $= 0.7$ nanometers

Lamp Current =10 milliamps Signal averaging time $= 2$ seconds Optimum Concentration = $0.2 - 20$ mg/L Sensitivity = $55 \text{ @ } 1 \text{ mg/L}$ Noise 0.5 (in the middle of the optimum range) Detection Limit = 0.003 mg/L

Testing Procedures:

- 1) All 100 mL volumetric flasks with ground-glass stoppers were rinsed with dilute HCI, three times with tap water, then three times with type 1 water.
- 2) Raw sample water from each sample site was vacuum aided filtered through a 0.45 micron filter with the suction apparatus rinsed three times with type 1 water between each sample.
- 3) The standard stock concentration was prepared by drop wise application into 250 mL plastic bottles. The amount of 1000 mg/L Ca stock added is indicated by the weight values reported in stock used (g) vs. resultant absorbance readings are in the alkalinity spreadsheets (in step 7) and used throughout this study.
- 4) Tarred, dry flasks were filled in the following manner:

Blk1) 100 mL type 1 water Blk2) 100 mL type 1 water

- A1) A weighed portion of Gladfelter Pond sample and weighed portion of type 1 water to \sim 100 mL resulting in a range of values from a \sim 10:1. to 20:1 dilution.
- A2) A weighed portion of Gladfelter Pond sample and weighed portion of type 1 water to \sim 100 mL resulting in a range of values from a \sim 10:1. to 20:1 dilution.
- 81) A weighed portion of Ross Spring sample and weighed portion of type1 water to \sim 100 mL resulting in a range of values from a \sim 10:1. to 20:1 dilution
- 82) A weighed portion of Ross Spring sample and weighed portion of type1 water to \sim 100 mL resulting in a range of values from a \sim 10:1. to 20:1 dilution
- C1) A weighed portion of Kahola Lake sample and weighed portion of type 1 water to \sim 100 mL resulting in a range of values from a \sim 10:1 to 20:1 dilution
- C2) A weighed portion of Kahola Lake sample and weighed portion of type 1 water to \sim 100 mL resulting in a range of values from a \sim 10:1 to 0:1 dilution
- 01) A weighed portion of Kahola Spring sample and weighed portion of type 1 water to \sim 100 mL resulting in a range of values from a \sim 10:1. to 20:1 dilution
- 02) A weighed portion of Kahola Spring sample and weighed portion of type 1 water to \sim 100 mL resulting in a range of values from a \sim 10:1 to 20:1 dilution.
- 5) 500 micro L of a LaCI3 (as a releasing agent) + HN03 (as a preservative solution was added to each flask.

Chloride:

The test for chloride (CI -) was conducted by titration of silver nitrate into a beaker in the presence of a electrochemical cell that measures the activity of the Ag+ ion, with cell potential as a function of titrant added. A calculated amount of KCI was used as a standard. The equipment used to measure the mV potential was a Horizon Ecology Co. model 5998-10. Both a silver billet and glass pH electrodes were used, as well as a magnetic stirring apparatus.

Testing Procedures:

1) Reagents were prepared:

A) Silver Nitrate titrant: 0.007 M: 1.2 g AgN03 in 1000 mL type 1 water, and was stored in a brown glass bottle

B) KCI standard: 0.005 M: was 0.3728 g KCI in 1000 mL type 1 water

C) 6 M HN03

2) All 200 mL beakers were rinsed with dilute nitric acid, rinsed three times with tap water, then rinsed three times with type 1 water.

- 3) The tarred, dry beakers, one sample at a time were filled then the weights were recorded (Step 6).
- 4) 2 500 ml amounts of 6 M 6 M HN03 were micropipetted into each beaker
- 5) A clean magnetic capsule was dropped into the beaker, the beaker was placed onto the magnetic stirrer with a piece of thin cardboard between the beaker and the metal plate of the magnetic stirring device.
- 6) The probe package was lowered into the beaker, with the initial mV, endpoint mV, titrant added, and values recorded, mV, and titrant added, and sample weight tables were generated.

Nitrate/Nitrite:

The Hach Method colorimetry test for the two most common forms of nitrogen in water, $NO₂$ and $NO₃$ were performed on a GCA/McPherson Instrument - model EU 700 series monochromator. The reacting products produce a bright pinkish red in the presence of nitrogen that is analyzed at 543 nanometers. The nitrate $NO₃$ is reduced to nitrite $NO₂$ by the cadmium and reagents then are analyzed, therefore with this test it was impossible to separate relative concentrations of each with this test and it was reported as mg/L of $NO₂$. and $NO₃$ Nitrogen. Nitrate ($NO₃$) is especially toxic to human and animal infants where the nitrogen molecule prevents $O₂$ uptake by the blood. The resulting condition is known as methemoglobinemia or "blue baby syndrome". The limit set (maximum contaminate level – MCL) by officials in Kansas for $NO₂$ and $NO₃$ as N is 10 mg/L. There is a high degree of probability that concentrations greater

than this limit are caused by anthropogenic influences such as excessive nitrogen fertilizer applications to crop lands, runoff from animal waste holding pits, or septic systems.

Testing Procedures:

- 1) All centrifuge tubes with caps, pipettes, vacuum aided suction apparatus, and mixing flasks were washed with dilute HCI, rinsed three times with tap water, then rinsed three times with type 1 water and allowed to dry.
- 2) Raw sample water from each sample site was vacuum aided filtered through a 0.45 micron filter with the suction apparatus rinsed three times with type 1 water between each sample.
- 3) Nitrate and Nitrite Hach Method Reagents and Standards were prepared: A) Nitra Ver 6 (tm) reagent packets: (Hach Chemical Company). The individual packets were marked "Nitrate LR, M00061" which is the MDSD number.
	- B) Nitrate stock solution: 500 mg/L N: 0.9205 g oven dried KN03 in 250 mL type 1 water.
	- C) NED Solution: To 200 mL type 1 water, 25 mL 85% H3P04 and 2.5g sulfanilamidime is added. This was stirred until the crystals dissolved, then 0.250 g N-(1-napthyl)-ethylenediamine (NED) is added. It needs to be stored in a refrigerator, and has a shelf life of one month.

4) Centrifuge tubes were filled in the following manner:

Blk1) One Nitra Ver 6 (tm) reagent packet,

Std1) One Nitra Ver 6 (tm) reagent packet, 100 micro L of 500 mg/L nitrate stock, 20 mL type 1 water

- A1) One Nitra Ver 6 (trn) reagent packet, 20 mL Gladfelter Pond sample by pipette
- B1) One Nitra Ver 6 (tm) reagent packet, 20 mL Ross Spring sample by pipette
- C1) One Nitra Ver 6 (tm) reagent packet, 20 mL Kahola Lake sample by pipette
- 01) One Nitra Ver 6 (tm) reagent packet, 20 mL Kahola Spring sample by pipette
- 5) The tubes were capped and shaken until all the powder from the reagent packets were dissolved
- 6) The tubes were centrifuged at 1/2 speed for 10 minutes
- 7) To produce the replicates the six tubes were then placed into a rack with a labeled empty tube next to each one and the following steps were performed:
	- A) 10 ml of Blk1 was pipette into Blk2, and 500 microliters NED solution was added to both
	- B) 10 ml of Std1 was pipetted into Std2, and 500 microliters NED solution was added to both
	- C) 10 ml of A1 was pipetted into A2, and 500 microliters NED solution

was added to both

- D) 10 ml of 81 was pipetted into 82, and 500 microliters NED solution was added to both
- E) 10 ml of C1 was pipetted into C2, and 500 microliters NED solution was added to both
- F) 10 ml of D1 was pipetted into D2, and 500 microliters NED solution was added to both

Orthophosphate:

The test for orthophosphate checks a sample for H_3PO_4 and its conjugate bases created by gains or losses of hydrogen ions up to and including PO_4^3 . This key nutrient for plants and algal growth can be indicative of a fairly balanced system when found at lower concentrations where it can operate as a limiting factor in plant growth. When higher concentrations are found, it can be a strong indicator of pollution which can cause explosive growth of algae and plants (with concentrations > 0.03 mg/L) that can cause a score of environmental problems including anoxia in water systems and fish kills. Two possible sources for this pollution could be agriculture runoff or domestic wastewater. This analysis was a colorimetric test performed on a Hach DR 3000 spectrophotometer.

Testing Procedures:

1) 50 mL volumetric flasks and ground glass stoppers, repeating dispenser, and glass pipettes were washed with dilute HCI, rinsed three times with tap water,

then three times with type 1 water and allowed to dry.

- 2) Reagents and standards were prepared
	- A) SULFURIC ACID: 2.5 M with 70 mL 12 M H_2SO_4 mixed slowly into 400 mL type 1 water, cooled, and diluted to 500 mL with type 1 water
	- B) MOLYBDATE SOLUTION: $20g$ (NH₄)₆Mo₇O₂₄ + 4H₂O, ammonium molybate, in 500 mL type 1 water
	- C) ANTIMONY SOLUTION: 1.10 g KSbOC₄H₄O₆ + 1/2 H₂O potassium antimony tartrate in 500 mL type 1 water, stored in the dark
	- D) ASCORBIC ACID SOLUTION: 1.06 g ascorbic acid in 60 mL type 1 water, prepared fresh daily
	- E) PHOSPHORUS STOCK SOLUTION: 100 mg/L as P: 0.4393 g oven dried KH2P04 diluted to 1000 ml type 1 water
- 3) The repeating dispenser was filled with 100 mL 2.5 M sulfuric acid, 10 mL antimony solution, 30.0 mL molybdate solution, in a 60 mL ascorbic acid solution.
- 4) The repeating dispenser was set at 8.0 mL and dispensed to each flask.
- 5) Raw sample water filter from each sample site was vacuum aided filtered through a 0.45 micron with the suction apparatus rinsed three times with tap water then three times with type 1 water before each extraction.
- 6) The flasks were filled in the following manner:

Blk1: 8 mL of reagent then filled to 50 mL line with type 1 water, weighed Blk1b: 8 mL of reagent then filled to the 50 mL line with type 1 water, and weighed again

- Std 1: 8 mL of reagent, 100 micro L of 100 mg/L concentration Phosphorus stock was micro-pipetted into the flask, weighed, flask tarred, then filled to the 50 mL line with type 1 water, and weighed again
- Std 1b: 8 mL of reagent, 100 micro L of 100 mg/L concentration Phosphorus stock was micro-pipetted into the flask, weighed, flask tarred, then filled to the 50 mL line with type 1 water, weighed
	- A1: 8 mL of reagent, then filled to the 50 mL line with Gladfelter Pond sample, weighed
	- A1b: 8 mL of reagent, then filled to the 50 mL line with Gladfelter Pond sample, weighed
	- 81: 8 mL of reagent, then filled to the 50 mL line with Ross Spring sample, weighed
	- B1b: 8 mL of reagent, then filled to the 50 mL line with Ross Spring sample, weighed
	- C1: 8 mL of reagent, then filled to the 50 mL line with Kahola Lake sample, weighed
	- C1b: 8 mL of reagent, then filled to the 50 mL line with Kahola Lake sample, weighed
	- D1: 8 mL of reagent, then filled to the 50 mL line with Kahola Spring sample, weighed
	- D1b: 8 mL of reagent, then filled to the 50 mL line with Kahola Spring

sample, weighed

- 7) A wavelength setting of 882 nm was set and the unit was turned on
- 8) The 1 cm. cell rinsed with type 1 water 3 times and the outside was wipe dry
- 9) After allowing for the unit to warm up, the cell was filled with type 1 water and the unit was zeroed.
- 10) The cell was emptied then filled with sample following the flask list (see #6) and the absorbance readings taken, with the cell being rinsed three times with type 1 water in between each filling
- 11) The weights and readings were then entered into tables

Zinc:

The tests for zinc content were all performed with a flame atomic absorption Perkin-Elmer AAnalyst model 100. To reach the optimum operating temperature for this procedure, all manual settings such as burner height and air/acetylene mix were adjusted to the maximum absorbance readings using a standard each time a test was run. The settings and ranges for these tests were;

Wavelength =213.9 nanometers

Slit Width = 0.7 nanometers

Lamp Current = 10 milliamps

Signal averaging time = 2 seconds

Optimum Concentration =0.05 - 2 mg/L

Sensitivity = 240 @ 1 mg/L

Noise 1.6 (in the middle of the optimum range)

Detection Limit = 0.005 mg/L

Testing Procedures:

- 1) 50 mL volumetric flasks and ground glass stoppers, repeating dispenser, and glass pipettes were washed with dilute HCI, rinsed three times with tap water, then three times with type 1 water and allowed to dry.
- 2) Standards were prepared:
	- Standard 1: 250 microliters of 1000 mg/L Zn stock micropipetted into 500 mL type 1 water
	- Standard 2: 500 microliters of 1000 mg/L Zn stock micropipetted into 500 mL type 1 water
	- Standard 3: 1 mL of 1000 mg/L Zn stock micropipetted into 500 mL type one water
- 3) Raw sample water from each sample site was vacuum aided filtered through a 0.45 micron filter with the suction apparatus rinsed three times with tap water then three times with type 1 water before each extraction.
- 4) The flasks were filled in the following manner:
	- Blk1) 50 mL of type 1 water
	- Blk2) 50 mL of type 1 water
	- Std 1a) 50 mL of Std 1 solution
	- Std1b) 50 mL of Std 1 solution
	- Std2a) 50 mL of Std 2 solution
	- Std2b) 50 mL of Std 2 solution
	- Std3a) 50 mL of Std 3 solution
	- Std3b) 50 mL of Std 3 solution
- A1) 50 mL of Gladfelter Pond sample
- A2) 50 mL of Gladfelter Pond sample
- 81) 50 mL of Ross Spring sample
- 82) 50 mL of Ross Spring sample
- C1) 50 mL of Kahola Lake sample
- C2) 50 mL of Kahola Lake sample
- 01) 50 mL of Kahola Spring sample
- 02) 50 mL of Kahola Spring sample
- 5) 250 micro L of $HNO₃$ was added to each flask as a preservative
- 6) The flame atomic adsorption tests were performed

Chapter Three

Field Study Results

Section 3A: Water Analysis Tests

Chloride Results:

During the second and third rounds of samples a great deal of drift in the mV values was experienced on the LED display as the silver nitrate was incrementally added. Therefore, only recorded the beginning and ending burette readings and initial mV reading and the approximate endpoint value of \sim 250 mV were recorded. It was realized in data entry phase using the Quattro Pro chloride template that at least 3 separate methodological problems had occurred:

- 1) During the initial round of samples, the temperature of the sample was taken by probe analysis - which reflected a fairly normal room temperature. During the second and third round of samples, this step was omitted by accident. This precludes the ability to correct for temperature.
- 2) During the second and third rounds, the refrigerated samples were poured into the tarred beaker, and the analysis by titration was performed. The sample was not allowed sufficient time to equilibrate to room temperature. This alters the conditions of the testing and precludes the ability to compare the chloride data from the second and third rounds of tests to the first round.
- 3) Only recording the initial and endpoint burette mL and mV values vs. incremental values does not allow for accurate evaluation of the both the linearity and accuracy of the results. This procedural error precludes the use of the chloride data as a whole.

All spreadsheet and data tables generated during the testing can be found in Appendix A. The results of testing for all three rounds of sampling were graphed in three different ways. The first was by the individual tests at the individual sites. The individual data points are illustrated in these graphs and can be found in Appendix B. The second set of graphs depict the results for all of the sites on a single test basis and compare these results to the State of Kansas Maximum Contaminant level (MCl) where applicable. The MCl values for zinc and nitrate/nitrite (as N) were set at 5 mg/L and 10 mg/L respectfully for drinking water. Orthophosphate concentrations greater than 0.030 mg/L can cause algae blooms that can cause hypoxia in the water body.

Zinc Results:

All concentrations measured in samples collected at all three sampling periods were well below the maximum contaminant level (MCl) of 5 mg/L. The highest concentrations were detected in the January $5th$ sample from Gladfelter Pond. The remaining analyses from other sites resulted in relatively low but steady concentrations.

Figure 17: Graph showing temporal changes in Zinc concentrations at all four sampling sites.

Orthophosphate Results:

All concentrations measured in samples collected at all three sampling periods were well below the 0.030 mg/L algal bloom level except for the measurement performed on the January 5th sample from Gladfelter Pond. It showed a spike in orthophosphate that was four times the concentration level needed to produce an algal bloom. The remaining analyses from other sites resulted in relatively low but steady concentrations. In fact concentrations of

orthophosphate measured in samples from Kahola Spring and Kahola lake were nearly identical for the duration of the study.

Figure 18: Graph showing temporal changes in Orthophosphate concentrations at all four sampling sites.

Nitrate/Nitrite (as N) Results:

All concentrations measured in samples collected at all three sampling periods were well below were below the MCL for nitrate-nitrogen that is 10mg/L. **While concentrations of nitrate were very low for all samples, there was a**

consistently higher concentration of nitrate measured in samples taken from Ross Spring as compared with the other three sample sites for the duration of the study. It was also noteworthy that nitrate concentrations were extremely steady with little temporal variability.

Nitrate/Nitrite Values

Figure 19: Graph showing temporal changes in Nitrate/Nitrite concentrations at all four sampling sites.

pH Results:

Measurements of pH indicated that all measurements were above 7 which is to be expected considering the abundance of buffering material commonly

found at both locations. It is probably not appropriate to use the data in graph to draw too many conclusions because there may have been a problem in the analytical method or equipment used which will be discussed later in the interpretation section.

Sample pH Measurements

Figure 20: Graph showing temporal changes in pH at all four sampling sites.

Alkalinity Results:

The alkalinity values derived from all analyses indicate as expected that alkalinity levels in the springs were significantly higher than those measured in the surface water during all sampling periods. It is noteworthy that the changes in alkalinity for the springs between the second and third round of sampling greater than those measured in the surface water bodies. It is also noteworthy that the alkalinity of Kahola Lake is greater than that measured at Gladfelter Pond.

 $CaCO₃$ Results:

The concentrations used in this graph were derived from the alkalinity tests by multiplying the base alkalinity values by fifty to arrive at the mg/L concentrations used in this graph. As might be expected the CaCO₃ concentrations mimic the alkalinity results indicating the strong relationship between CaCO₃ content and alkalinity.

Figure 22. Graph showing temporal changes in CaCO₃ concentrations at all four sampling sites.

Calcium Results:

This graph appears to show differences between concentrations measured in samples from the springs as compared to those measured in samples from the surface water bodies. As expected, the direct contact with the limestone bedrock provides the springs with a source for calcium resulting in higher concentrations. Also, the changes in the spring water concentrations are much more dynamic than those measured in samples from surface water bodies.

Figure 23: Graph showing temporal changes in Calcium concentrations at all four sampling sites.

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Temperature Results:

This graph shows how the two spring locations are able to maintain a higher water temperature at least partially due to the insulation provided by the heavy soils and bedrock. Also in the graph there is a predictable pattern of larger temperature swings at Gladfelter Pond than at Kahola Lake. These changes in temperature appear to be more extreme and occur more quickly at Gladfelther Pond than at Kahola Lake possibly due to the larger water volume at Kahola Lake.

Sample Temperature Graph

Results arouped by site:

The next set of graphs were created by grouping the results from the temperature, pH , alkalinity, CaCO₃, and free calcium tests on a site by site basis. While the magnitudes of test results varied somewhat from site to site, the same basic pattern of temporal variability can be seen in each of four graphs below (Figure 25). The most striking similarities were found in the free calcium and $CaCO₃$ results. Notice that the CaCO₃ concentrations were highest and the free calcium concentrations were lowest in samples collected on January 5th.

Figure 25. Graphs of temperature, pH, alkalinity, CaCO₃, and free calcium grouped by site.

Graphs of the zinc, orthophosphate, and nitrate/nitrite (as N) concentration data were also grouped on a site by site basis (Figure 26). Notice that the concentrations of Zinc were most variable at all sampling sites except Ross Spring. In fact all three constituents were relatively steady in concentration at Ross Spring. This was not the case however at Kahola Spring, where concentrations of zinc and nitrate and nitrite appear to vary much more. It is important to note that the absolute magnitude of this variability is relatively small.

mg/L concentrations

Nov. 11,1999

Jan 5,2000

Nov. 11,1999

Jan 5,2000

Feb. 7, 2000

Feb. 7, 2000

Section 38: Site Investigations of Geology and Hydrology

It was the purpose of the site investigations to examine the limestone joint patterns at both springs with reference to water flow direction predicted in the Regional Bedrock Geology section seen in Figure 4 (pg. 6). One morning after a steady but light rainfall event, a study was conducted of the specific joint system at Ross Spring. A steady discharge of water from Ross Spring was observed emanating from a joint in the Neva limestone. A small "u" shaped groove in the ground was observed at the spring. This groove appeared to be caused by the same joint from which the spring was flowing. The directional trend of the surface expression of the joint was toward the southwest. The dimensions of the groove itself varied from one to three centimeters across and one to three centimeters deep, leading uphill to the southwest at a compass bearing of 220°. The surface expression of the groove was in some places not readily visible but it could be felt through soft-soled waterproof boots. In this way it could be traced uphill about 50 meters from the spring. Where the Neva limestone was shallow or exposed the joint could be easily seen following this same southwesterly trend. It was concluded that this particular limestone joint was the primary flow path for groundwater that eventually flows out of Ross Spring.

Another type of site investigation used at RNHR was kite aerial photography. Figure 27 is a kite aerial photo of the building complex and newly constructed sewage lagoon at RNHR. The significance of this view in the context of Ross Spring is that this area is both upgradient and in the vicinity of the particular joint from which Ross Spring appears to flow.

Figure 27: Kite Aerial Photograph shows the building complex area and newly constructed sewage lagoon at the Ross Natural History Reservation. Taken by the author and Or. J. S. Aber, in the fall of 1999

In the vicinity of Kahola Spring the orientation of the joints in the limestone was not as visible as at RNHR, but upon closer inspection two preferred orientations of joints that could be influencing water flow to the spring were observed. The observed orientation of the first joint set was similar to that observed at Ross Spring. It trended from southwest (230°) to northeast (50°). The second preferred orientation of joints trended from northwest (320°) to southeast (140°).

Chapter Four

Interpretation of Results

The first step in the interpretation of my results was to compare my values with values obtained in previous studies. A water chemistry study and resulting Master's Thesis for the Earth Science Department was authored by Thomas Peterson in December 1992 entitled, Water Quality in Lake Kahola and Adjacent Domestic Water Wells. Three of his sampling sites were identical to three of mine; 1) Ross Spring, 2) Kahola Lake (specifically at Cabin 93), and 3) Kahola Spring. At each of these sites, four tests were identical; 1) Calcium, 2) orthophosphate, 3) pH, and 4) Temperature.

Also in this thesis values were included from two separate water quality studies performed by the Kansas Department of Health and Environment (KDHE) at Kahola Lake. One study was done in 1986 and one in 1990. Three of the tests in the KDHE studies were identical to those in Peterson (1992) and the current project: 1) Calcium, 2) Orthophosphate (next section), and 3) pH. The values from the previous studies and my results (estimate of error is $+$ or $-$ about 3% overall - except chloride) were entered into Excel Spreadsheet for graphical comparison.

Calcium Comparison

In the first round of sampling and analysis, a significant elevation of free calcium was measured as compared to previous studies. Note that by the second round of testing there was a decrease in the calcium concentrations at all three

sampling sites, possibly as a result of the precipitation in the region (Figure 28). However, these values are still higher than what was seen in the previous studies

Overall Calcium Trend Comparison

Figure 28: Graph comparing the calcium analysis results of this study with previous studies.

pH Comparison

The measured pH values from the current study have apparently remained virtually unchanged from previous studies (Figure 29). This is probably at least in part a function of the buffering capacity of the system being studied. It should be noted that confidence in the pH measurements in this study is low due to possible equipment problems,

Overall pH Trend Comparison

Figure 29: A graph comparing the measured pH values from the current study with previous studies.

Temperature Comparison

The results of this study show a similar trend when the corresponding time frames from the previous study and my values were compared (Figure 30). Kahola Lake temperatures exhibit a greater sensitivity to seasonal changes in temperature as compared to the somewhat less variable temperatures measured at the Springs. This makes sense since surface water bodies tend to change temperature more rapidly than groundwaters in the subsurface.

Overall Temperature Trends

Figure 30: A graph comparing the measured temperature values from the current study with previous studies.

Orthophosphate Comparison

Orthophosphate concentrations measured in this study were higher than those measured in previous studies (Figure 31). It is important to note however, that concentrations of orthophosphate depicted in this graph are relatively low in all cases. This is not surprising given that most of the recharge areas for the springs and the drainage area for Kahola Lake are pasturelands which are probably not fertilized. It also appears that the septic systems around the lake are functioning properly so that orthophosphates are not flowing from them into the Lake in significant quantities. That is not to say that continued monitoring is not warranted since concentrations did appear to be somewhat higher in this study as compared with previous studies.

Overall Orthophosphate Concentration Comparison

Figure 31: A graph comparing the measured orthophosphate concentrations from the current study with previous studies.

In summary a few statements can be made based on the results from the limited number of samples tested in this study. As expected the concentrations of calcium and $CaCO₃$ were significantly higher in both springs versus the two surficial water bodies. In addition, Kahola Lake concentrations were higher than those measured at Gladfelter Pond. This was probably due to two factors. 1) Calcium and $CaCO₃$ rich groundwater from springs discharging into Kahola Lake. 2) The prevalence of limestone rocks in the drainage basin in which the Lake was constructed.

Since constituents such as calcium seem to be affected by antecedent moisture conditions, this factor should be accounted for in future comparisons

with historical data. Lacking this, it can only be speculated that the significantly higher values found in the first round of my testing were probably caused by the extreme lack of precipitation in the days previous to the sampling. When comparing my results for both calcium and alkalinity (therefore $CaCO₃$) on a site by site basis the same pattern was repeated at all four sites - the alkalinity (therefore $CaCO₃$) increased during the second round of testing while the free calcium ions decreased in concentration. In a closed system this could be explained as a shift in the equilibrium equation: $\text{CaCO}_3 + \text{H}_2\text{CO}_3 \longleftrightarrow \text{Ca}^{2+} +$ $2HCO₃$. However, all four of these locations are open systems that allow influences from outside sources. While some of the repeating pattern may be due

to the normal shift in the equilibrium equation, I believe that the increased $CaCO₃$ content is due to the observed increase in water volume flowing through the aquifer that may flush out the disolved limestone particles from the bedrock. At the same time the increased water volume is diluting the concentration of the free calcium ions.

The alkalinity results followed a predictable trend that followed the logic that the values obtained from the springs would be similar in nature and would be higher than the surficial values. The pH values for Ross Spring were lower, or more acidic, than Gladfelter Pond - directly contradicting my alkalinity values. Therefore, I have a serious doubt about the accuracy and precision of the measured pH values when compared to the titrated alkalinity values that produced a logical and predictable pattern. When my pH readings were graphed with the values obtained from previous studies, the results (therefore the

systems) appear both logical and steady state. This may be misleading and should be either viewed skeptically or totally disregarded.

The third goal of the water analysis involved looking for some chemicals that should not present above background levels in these systems naturally. The specific constituents in this category were nitrate/nitrite, phosphate, and zinc. The results of the tests for nitrate/nitrite and zinc showed levels to be far below the MCL standard for drinking water.

There is an interesting phenomenon occurring with the Ross Spring nitrate/nitrite results. The level holds very steady at nearly 1 mg/l and does not drop or rise as some of the other tests do with the January recharge.

There was also a low but steady concentration of zinc observed throughout the study at Ross Spring. The concentrations of zinc may be indicating a small but steady pollution point source somewhere upgradient along the limestone joint system described earlier. There are also zinc spikes at Gladfelter Pond, Kahola lake, and Kahola Spring during the second round of testing. This would tend to cause speculation that this could be related to precipitation events but there is not enough data to draw any firm conclusions about the source of the zinc.

Some other important observations from this study are listed below:

1) Minor amounts of precipitation interrupting periods of aridity appear to cause fluctuations in different chemical concentrations. Despite the limited time frame of this study, It is believed that the data from this study may contradict

the "steady-state" image about Flint Hills springs. The shifts in alkalinity and calcium ion concentrations were much greater in the springs versus the surficial bodies which supports this hypothesis.

- 2) The only test that appeared to support the steady state picture of the Flint Hill Springs was temperature. The values appeared to support the logical theory that there is less temperature variation within aquifers as compared to surface water bodies. Also the size or volume of a surface water body appears to affect the magnitude of temperature variations it will exhibit. Therefore the temperature of Kahola Lake seems to be less variable than that at Gladfelter Pond.
- 3) Groundwater flow patterns seem to be strongly affected by joint patterns at both Kahola Lake and RNHR.

Chapter Five

Conclusions

It was the purpose of this study to examine selected chemical and physical properties of the ground water and surface water at two locations in east central Kansas. These two locations were the Ross Natural History Reservation and the Kahola Lake area.

The first step in the study involved doing a background investigation for precipitation and previous test data. The precipitation data showed that there was virtually no precipitation in the time period immediately prior to the study. This data also indicated minimal amounts during the study period. The second step in this study was field studies.

The second component of the study was water sampling and testing. The specific tests conducted were temperature, pH , calcium, alkalinity, CaCO₃, chloride, orthophosphate, nitrate/nitrite ($NO₂$ and $NO₃$ as N), and zinc from fall 1999 through winter 2000. The test results for chloride were deleted due to three separate procedural errors.

With the tests for temperature, pH , calcium, alkalinity, and $CaCO₃$ my primary interest was evaluating the differences in values, especially the relative changes in the values between the surficial water bodies (being Gladfelter Pond and Kahola Lake) verses the spring water values (being Ross and Kahola Springs). The results of these tests showed that there were greater shifts in chemical concentrations in the spring water values than the surficial water bodies even with minimal precipitation. The only values obtained in my study that

indicated that the spring values were more stable, i.e. slower to change than the surficial values was temperature. This result was expected because of the insulating influence of the bedrock and regolith. The alkalinity and therefore the calculated CaCO₃ content and the calcium content showed a distinct trend at all four locations. As the CaCO₃ content increased $-$ the calcium decreased. In a closed system this could be explained by the chemical equation $CaCO₃ + H₂CO₃$ $Ca²⁺ + 2HCO₃$. While this trend may be a reflection of a shift in this equilibrium equation these are open systems. I believe that the slight precipitation encountered after the first round of testing was sufficient to put a volume of limestone particles (disolved solids from the limestone bedrock) into suspension while simultaneously decreasing the dissolved calcium concentration due to the increased water volume.

The tests for nitrate/nitrite ($NO₂$ and $NO₃$ as N) and zinc revealed that all the levels for both nitrate/nitrite and zinc were below the Kansas MCl levels for drinking water. However, there were spikes in the zinc concentration levels at both Kahola sites of about 0.2 mg/l and 0.9 mg/l and at Gladfelter Pond during the second round of testing again possibly due to the slight increase in precipitation forcing more zinc into solution from an unknown source. There is not enough data to speculate on the origin of the zinc at these three locations. At Ross Spring there was a fairly steady concentration of zinc just under 1 mg/l throughout the course of the study. Due to the orientation of the limestone joint system which feeds this spring, I believe that the source of the zinc may be in the area to the north of the building complex.

There was a significant spike in the orthophosphate concentration at Gladfelter Pond during the second round of testing, at a level that greatly exceeds the amount necessary to cause algal blooms. The source of this spike in concentration is not known.

In retrospect, there are several other areas of inquiry that would have increased the effectiveness of this study:

- 1) Water flow measuring at the springs and water level elevation measurements at the surficial sites.
- 2) Precipitation measurements at the two sites.
- 3) Geo-physical studies (electrical resistively) at the two locations to determine bedrock orientations in a non-invasive manner.
- 4) Total ion water studies over an extended period of time.
- 5) A detailed soil study including profile descriptions. testing for pollutants and measurements of infiltration rates.
- 6) A greater range of checks for metals and compounds such as atrazine and the daughter products of DDT.

In summary. despite the limited timeframe of this study there was a considerable amount of spatial and temporial variation found in the various water properties between all the study sites. It was also found that slight changes in factors such as precipitation dramaticaly changed the different hydrologic systems.

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Appendix A

Data Tables and Spreadsheets

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unk. meq/L

unk. meq/L

Nitrate/Nitrite Weights and Absorbance Tables by Sample Date

The nitrate/nitrite stock solution was determined to be a concentration of 500 mg/L. This did not change through the course of the study.

Therefore, the averaged concentration of the standard is 2.5 mg/L. This allows calculations of mg/L concentrations of the unknowns through the use of Beers Law by the equation:

The final column is the result of insertion of the variables in the equation, with the Abs. reading for each site the result of averaging the mean values at each site sample with the replecate. The value is reported in mg/L.

Std Calculations $Cs = 500$ mg/L x (0.1 mL/20 mL) $Cs = 2.5$ mg/L

Therefore, the averaged concentration of the standard is 2.5 mg/L. This allows calculations of mg/L concentrations of the unknowns through the use of Beers Law by the equation:

Sample date: Feb. 7, 2000
Tube weight weight **Absorbance Readings: Mean** Blk: 20.0g .003 .006 .004 .003 .004 Std: 0.1g (100 micro L) in 20g type 1 2.320 2.155 2.255 2.187 2.251

Std Calculations $Cs = 500$ mg/L x (0.1 mL/20 mL) $Cs = 2.5$ mg/L

Therefore, the averaged concentration of the standard is 2.5 mg/L. This allows calculations of mg/L concentrations of the unknowns through the use of Beers Law by the equation:

Orthophosphate Absorbance and Concentration Tables

The phosphate stock solution was determined to be a concentration of 100 mg/L. This did not change through the course of the study.

Sample date: Nov. 11, 1999 Flask weight Absorbance Readings: Mean Calc.S B11: 49.266 9 .002 .001 .002 .002 .002 .002 .001 Blank Avg. B11b: 49.605 9 .003 .001 .004 .002 .003 .003 .002 .002 wt.P stock total wt. **Mean Calc.S** Std 1: 0.099 9 49.181 9 .296 .296 .297 .302 .298 .298 .002 Std. Avg. Std 1b: 0.096 9 49.503 9 .292 .294 .296 .298 .294 .295 .002 .297 Std 1 calculations Std 1b calculations $Cs = 100$ mg/L x (0.099mL/49.181) $Cs = 100$ mg/L x (0.096mL/49.503)
 $Cs = 0.201$ mg/L $Cs = 0.194$ mg/L $Cs = 0.201$ mg/L

Therefore, the averaged concentration of the standard is .198 mg/L. This allows calculations of mg/L concentrations of the unknowns through the use of Beers Law by the equation:

Flask weight Absorbance Readings: Mean Calc.S B11: 49.424 9 .002 .004 .002 .003 .005 .003 .001 Blank Avg. B11b: 49.766 9 .003 .004 .005 .004 .005 .004 .001 .004 wt.P stock total wt. **Mean Calc.S** Std 1: 0.098 9 50.010 9 .302 .299 .300 .302 .304 .301 .001 Std. Avg. Std 1b: 0.102 9 49.892 9 .294 .294 .301 .296 .298 .297 .003 .299 Std 1 calculations Std 1b calculations
Cs = 100mg/L x (0.098mL/50.010) Cs = 100mg/L x $Cs = 100$ mg/L x (0.098mL/50.010) $Cs = 100$ mg/L x (0.102mL/49.892)
 $Cs = 0.194$ mg/L $Cs = 0.194$ mg/L

Therefore, the averaged concentration of the standard is .195 mg/L. This allows calculations of mg/L concentrations of the unknowns through the use of Beers Law by the equation:

> $Cx = Cs (Ax - Ab)$ where: $Cx = concentration of the unknown$ (As - Ab) Cs = concentration of the standard $Ax = Abs$. reading of the unknown As = Abs. reading of the standard Ab =Abs. reading of the standard

Sample date: Feb. 7, 2000 Flask weight Absorbance Readings: Mean Calc. S 811: 49.266 9 .003 .005 .004 .004 .005 .004 .001 Blank Avg. B11b: 49.605 9 .006 .005 .008 .010 .007 .007 .002 .003 wt.P stock total wt. Mean Calc.S Std 1: 0.101 9 49.358 9 .296 .301 .302 .300 .304 .301 .003 Std. Avg. Std 1b: 0.098 9 49.659 9 .294 .296 .298 .289 .280 .291 .004 .296 Std 1 calculations Std 1b calculations $Cs = 100$ mg/L x (0.101 mL/49.358) $Cs = 100$ mg/L x (0.098 mL/49.659)
 $Cs = 0.196$ mg/L $Cs = 0.200$ mg/L $Cs = 0.200$ mg/L

Therefore, the averaged concentration of the standard is .198 mg/L. This allows calculations of mg/L concentrations of the unknowns through the use of Beers Law by the equation:

> $Cx = Cs (Ax - Ab)$ where: $Cx = concentration of the unknown (As - Ab)$ $Cs = concentration of the standard$ $Cs = concentration of the standard$ $Ax = Abs$. reading of the unknown As =Abs. reading of the standard Ab = Abs. reading of the standard

Appendix B

Graphs With Data Points On A Single Test

At A Single Site Basis

Gladfelter Pond Alkalinity Values

Kahola Spring Alkalinity Values

Calcium Test Results

Gladfelter Pond Calcium Concentrations

Ross Spring Calcium Concentrarions

Kahola Spring Calcium Concentrations

Nitrate/Nitrite (as N) Test Results

Gladfelter Pond Nitrate/Nitrite Values

Ross Spring Nitrate/Nitrite Values

Kahola Lake Nitrate/Nitrite Values

Gladfelter Pond Orthophosphate Concentrations

Ross Spring Orthophosphate Concentrations

Kahola Lake Orthophosphate Concentrations

Kahola Spring Orthophosphate Concentrations

pH Test Results

11/11/99 115/00 2/7/00

Temperature Test Results

Gladfelter Pond Temperature

 0.15 $0,1$

 $0.05 -$

 $\mathbf{0}$

Nov. 11,1999

Jan. 5,2000

Sample Dates

Feb. 7, 2000

Gladfelter Pond Zinc Concentrations

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A STUDY OF THE CHEMICAL AND PHYSICAL PROPERTIES OF THE GROUND WATER AND SURFACE WATER AT ROSS NATURAL HISTORY RESERVATION AND KAHOLA LAKE **IN** EAST- CENTRAL KANSAS Title

Signature of Graduate Office Staff

 2000 Date Received **by the U**

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